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EPR SPECTRA AND π-ELECTRONIC STRUCTURES OF ANION RADICALS OF A NITRO-SUBSTITUTED INDOLINE SPIROPYRAN

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UDC 543.422.27 + 541.515'138 +
547.754'814

Electrochemical generation was used to obtain anion radicals of 1,3,3-trimethyl-5-nitrospiro(indoline-2,2'-[2H]chromene), and their EPR spectra in acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were recorded. On the basis of an analysis of the hyperfine structure (hfs) of the EPR spectra it was concluded that, as a consequence of the relatively weak interaction of the π-systems of the indoline and benzopyran fragments, cleavage of the bond between the spiro carbon atom and the oxygen atom in the pyran ring does not occur in the formation of the anion radical, and the additional unpaired electron is delocalized in the π-system of the indoline fragment of the molecule.

The utilization in science and technology of materials based on spiropyrans is due mainly to the capacity of many of them to form colored products under the influence of UV light and ionizing radiation [1]. From the photochromic transformations of spiropyrans, the accumulated experimental data make it possible to draw rather convincing conclusions regarding the processes that take place under the influence of UV light, which are due to cleavage of the bond between the spiro $C_{(2)}$ carbon atom and the oxygen atom in the pyran ring and lead to the formation of the merocyanine form, which absorbs in the longer-wave region as compared with the starting spiropyran [2].

Individual communications, on the basis of which it is difficult to create a complete representation of the mechanism of the formation of colored compounds, are available regarding the transformation of spiropyrans under the influence of ionizing radiation. Researchers have noted that the colored products that develop during the radiolysis of spiropyrans have absorption spectra that differ from the spectra of the corresponding merocyanine forms [3]. In this connection, a question arises as to whether the development of colored products that differ from the merocyanine forms is due to interaction of the latter with the products of radiolysis of the matrix or whether the transformation of the spiropyran under radiolysis proceeds through a step that bypasses the formation of the merocyanine form. Pulse radiolysis has established [4, 5] that anion radicals of spiropyrans, which are subsequently protonated, are formed in the case of irradiation of indoline spiropyrans in ethanol solution with an electron beam. The data obtained in an investigation by EPR of the radiolysis of an unsubstituted indoline spiropyran — 1,3,3-trimethylspiro(indoline-2,2'-[2H]chromene) (I) — in a vitreous ethanol solution at 77°K [6] also constitute evidence for the formation of anion radicals of a spiropyran and their subsequent protonation, which leads to the formation of free radicals. The EPR spectra of free radicals were obtained in the solid phase and had a resolution that did not make it possible with absolute certainty to establish the structures of the radicals. Attempts to obtain anion radicals of unsubstituted spiropyran I by electrochemical generation in the liquid phase in aprotic solvents were unsuccessful. Polarographic investigations established that its first reduction wave ($E_{1/2} = -2.49 \pm 0.01$ V) is irreversible, in connection with which, we were unable, by using a stationary method, to accumulate anion radicals in concentrations necessary for recording of the EPR spectra.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow, 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1477-1481, November, 1984. Original article submitted August 8, 1983.

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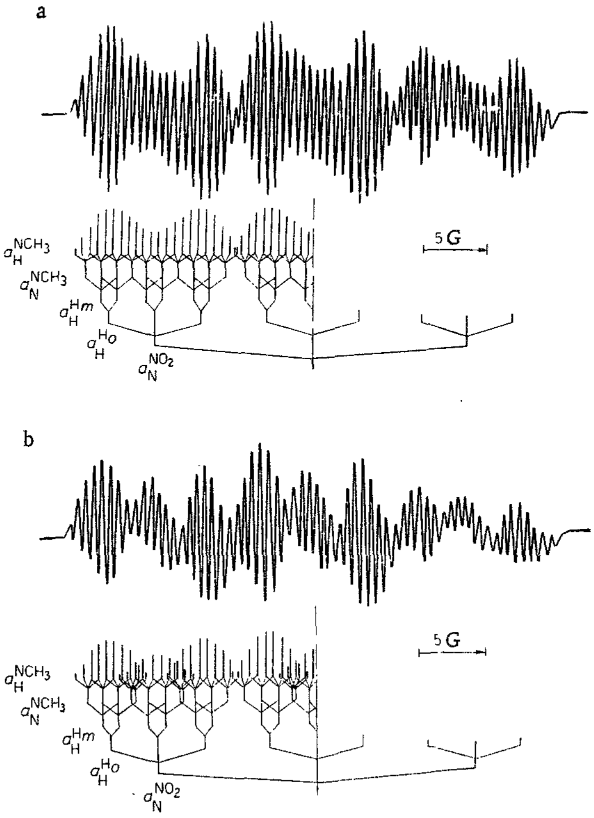
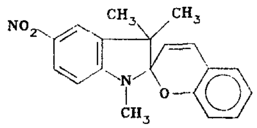


Fig. 1. EPR Spectrum of the anion radicals of 1,3,3-trimethyl-5-nitrospiro-(indoline-2,2'-[2H]chromene (II) in acetonitrile (a) and DMF (b) and its reconstruction in the region of low magnetic fields.

In order to obtain the EPR spectra, establish π-electronic structures of the anion radicals, and to shed some light on the problem as to whether the cleavage of the bond between the spiro $C_{(2)}$ carbon atom and the oxygen atom in the pyran ring we carried out electrochemical generation of anion radicals of a nitro-substituted indoline spiropyran — 1,3,3-trimethyl-5-nitrospiro(indoline-2,2'-[2H]chromene) (II) in aprotic solvents: acetonitrile, DMF, and DMSO.



II

The EPR spectra of the anion radicals of spiropyran II (Fig. 1) consist of 64 (in acetonitrile) and 62 (in DMF and DMSO) resolved lines of the hyperfine structure (hfs) grouped into a triplet with a splitting of ∿12 G. It might be assumed that the ratio of the intensities of the components of the triplet should be 1:1:1 and that the indicated splitting is due to coupling of the unpaired electron with the available spin, which is equal to unity, and the nucleus of the nitrogen atom of the electron-acceptor nitro group. The 1:1:1 ratio in the EPR spectra is not particularly completely satisfied: the intensities of the hfs lines of the extreme components of the triplet are lower as compared with the intensities of the lines of the central component. This is particularly noticeable in the region of high magnetic fields (Fig. 1) and in more viscous solvents (DMF and DMSO).

It is apparent from the spectra that each component of the triplet with a splitting of ≈12 G consist of three groups of hfs lines with an intensity ratio of 1:0.6:1 and a splitting of ∿3.6 G, which may be due to hyperfine coupling (hfc) of the unpaired electron either with one nitrogen atom nucleus or with two equivalent protons. The number of hfs lines in the component of the triplet with a splitting of 3.6 G is 10, and their intensity ratio amounts

TABLE 1. Parameters of the EPR Spectra of Anion Radicals of 1,3,3-Trimethyl-5-nitrospiro(indoline-2,2'-[2H]chromene) (II)

Solvent	Spectral length, G	Splitting constant, G					—*	—†
		$a_N^{NO_2}$	$a_H^{H_o}$	$a_H^{H_M}$	$a_N^{NCH_3}$	$a_H^{NCH_3}$		
CH_3CN	36,6 ±0,3	12,0 ±0,3	3,6 ±0,1	1,16±0,05	1,16±0,05	0,58±0,03	1,64±0,15	1,87±0,07
DMF	36,5±0,2	11,9±0,4	3,6±0,1	1,15±0,06	1,15±0,06	0,58±0,06	1,95±0,14	1,77 ±0,18
DMSO	36,1±0,3	11,6±0,4	3,6±0,1	1,17±0,03	1,17±0,03	0,59±0,02	2,54±0,15	1,74±0,07

*Ratio of the width of the hfs lines of the component at high field to the width of the hfs lines of the central component for the triplet with splitting constant $a_N^{NO_2}$.

†The ratio of the width of the hfs line of the central component to the width of the hfs lines of the extreme components for the triplet with splitting constant $a_H^{H_o}$.

to 0.9:3.1:5.1:7.2:8.1:7.9. If it is assumed that the splitting of 3.6 G is associated with the hfc of the unpaired electron with the nucleus of the nitrogen atom in the heteroring, the subsequent splitting of the hfs lines in the component of the triplet should be due to hfc with two groups of equivalent protons (with respect to the three protons in the group) with splittings of $\sim$1.2 and 0.6 G, inasmuch as in this case the number of hfs lines and their positions satisfactorily describe the experimental spectrum. However, the intensity ratio of the hfs lines in this case does not coincide with the experimentally measured value.

If the splitting of 3.6 G is associated with the hfc with two equivalent protons in the ortho positions relative to the nitro group, the observed hfs of the component of the triplet should be due to hfc with the nucleus of the nitrogen atom of the heteroring ($a_N^{NCH_3} \approx 1.2$ G), three equivalent protons of an N-methyl group ($a_H^{NCH_3} \approx 0.6$ G), and one proton in the meta position relative to the nitro group ($a_H^{H_m} \approx 1.2$ G). In this case the ratio of the intensities of the hfs lines in the component of the triplet with splitting constant $a_H^{H_o} \approx 3.6$ G virtually coincide with the experimentally observed value and amounts to 1:3:5:7:8:8. The latter assignment of the splitting constants is also confirmed by the results of investigations of the EPR spectra of the anion radicals of p-nitroaniline in acetonitrile [7], according to which the hfc constants for the nucleus of the nitrogen atom of the nitro group, the protons in the ortho and meta positions to the nitro group, and the nucleus of the amino nitrogen atom are, respectively, 12.18, 3.36, 1.12, and 1.12 G. Thus the positions of the hfs lines in the EPR spectra of the anion radicals of II are completely explained by the hfc of the unpaired electron with the nuclei of the atoms of the indoline fragment. Splittings due to hfc with the protons of the benzopyran fragments are not observed in the spectra.

The differences in the ratios of the intensities of the extreme components of the triplet with hfc constant $a_N^{NO_2} \approx 12$ G and the central component of the triplet with a constant of $a_H^{H_o} \approx 3.6$ G from the expected ratios of the amplitudes, respectively, 1:1:1, and 1:2:1, observed in the experimental EPR spectra are due to broadenings of the hfs lines. The considerably greater broadening of the hfs lines of the component of the triplet with hfc constant $a_N^{NO_2} \approx 12$ G at high field and the increase in the broadenings of the hfs lines of the extreme components of the indicated triplet as the viscosity of the solvent increases (Fig. 1 and Table 1) constitute evidence that the anisotropy of the Zeeman interaction and the dipole hfc with the nucleus of the nitrogen atom of the nitro group, which is not completely averaged as a result of retarded rotation of the anion radicals in the solvents used [8], makes the principal contribution to the broadening under consideration.

The solvent-independent ratio of the intensities of the components of the triplet with hfc constant $a_H^{H_o} \approx 3.6$ G, which is equal to 1:0.6:1 instead of the expected 1:2:1, is due to broadening of the hfs lines of the central component due to modulation in the antiphase of the isotropic hfc with two equivalent protons [8]. Modulation of the isotropic hfc is a consequence of intramolecular processes that lead to redistribution of the spin density between the carbon atoms in the ortho positions with respect to the nitro group. Thus vibrations of the nitro group and vibrations of the indoline and benzopyran fragments relative to one another may be intramolecular processes of this sort [9].

Thus it follows from an analysis of the hfs of the EPR spectra of the anion radicals of II that the degree of interaction of the π-systems of the indoline and benzopyran fragments is low, as a consequence of which, cleavage of the bond between the spiro carbon atom and the oxygen atom in the pyran ring does not occur in the formation of the anion radicals of II, and the additional unpaired electron is delocalized in the π-system of the indoline fragment of the II molecule. The hfc constants for the indoline fragment of the anion radical of II are close to the corresponding hfc constants for the anion radical of p-nitroaniline [7]. Proceeding from this, we evaluated the magnitudes of the spin densities in the anion radical of II using the known semiempirical ratios for the hfc constants in aromatic systems. In conformity with the McKonnell expression [10], to evaluate the spin densities on the carbon atoms in the 4, 6, and 7 positions ($\rho_C^{C(4,\ 6)}$ and $\rho_C^{C(7)}$) we used the dependence $a_H = Q_{CH}\rho_C^{\pi}$, in which the Q_{CH} parameter was assumed to be 25 G [11]. According to the Karplus-Fraenkel expression [12], the densities of the unpaired electron on the nitrogen and oxygen atom of the nitro group ($\rho_N^{NO_2}$ and $\rho_O^{NO_2}$) were evaluated using the expression $a_N^{NO_2} = Q_N^{NO_2}\rho_N^{NO_2} + 2Q_{NO}^{NO_2}\rho_O^{NO_2}$, in which $Q_N^{NO_2}$ and $Q_{NO}^{NO_2}$ were assumed to be 99 and −36 G, respectively, [13]. The spin density on the indoline nitrogen atom ($\rho_N^{NCH_3}$), in accordance with [14], was evaluated from the expression $a_N^{NCH_3} = Q_N^{NCH_3}\rho_N^{NCH_3}$, disregarding the effect on $a_N^{NCH_3}$ of the spin density on the carbon atom in the 7a position. The $Q_N^{NCH_3}$ value was assumed to be 25 G [14]. In our evaluations we assumed that the overall density of the unpaired electrons in the π system of the indoline fragments of the anion radical of II is equal to unity; the spin density on the carbon atom in the para position with respect to the nitro group is approximately equal to the spin density on the carbon atom in the ortho position; the spin density on the carbon atom in the meta position is negative [7]. For the spin densities we obtained the following approximate values: $\rho_N^{NO_2} \simeq 0.23$, $\rho_O^{NO_2} \simeq 0.15$, $\rho_C^{C(4,\ 6)} \simeq 0.14$, $|\rho_C^{C(7)}| \simeq 0.05$, and $\rho_N^{NCH} \simeq 0.05$.

EXPERIMENTAL

The anion radicals of spiropyran II were obtained by electrochemical reduction on the surface of a mercury drop in a microcell mounted directly in the resonator of the EPR spectrometer. The II concentration in solutions in acetonitrile, DMF and DMSO was $2.5 \cdot 10^{-3}$ mmole/liter; the concentration of the supporting electrolyte — tetra-n-butylammonium perchlorate — was 0.125 mmole/liter. The electrochemical generation of the anion radicals was carried out at potentials within the limits of the plateau of the limiting diffusion current of the first one-electron reversible polarographic waves ($E_{1/2} = -1.29 \pm 0.01$ V). The EPR spectra were recorded with a Soviet Rubin X-range spectrometer with a cylindrical resonator (resolution 0.1 G). Spiropyran II was synthesized by the method in [15] and was recrystallized repeatedly from acetonitrile and had mp 174°C. Purification of acetonitrile, DMF and DMSO was realized in accordance with known methods [16].

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